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(54) Hydrocarbon processing

(57) A process for the catalytic conversion of synthesis-gas into a product which comprises naphtha, kerosine and distillate is characterized in that the catalyst is a Fischer-Tropsch catalyst also containing a zeolite, the naphtha fraction contains 60% or less linear paraffins and the kerosine and distillate fractions contain more linear paraffins and olefins than found in the naphtha fraction. Reduction of the relative amount of straight chain material in the naphtha fraction increases the octane number and so enhances the quality of the gasoline product, while the high quality of the kerosine and distillate fractions is maintained.

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HYDROCARBON PROCESSING

5 ## Background of the Invention

This invention relates to improvements to the Fischer-Tropsch process for the conversion of synthesis-gas into hydrocarbons.

The Fischer-Tropsch process is a well known and
10 researched process for the conversion of mixtures of carbon monoxide and hydrogen, known as synthesis-gas, into hydrocarbons. The process is described in "Fischer-Tropsch and Related Synthesis" by H. Storch, N. Golumbic and R.B. Anderson, John Wiley and Sons 1951. A

more recent review of Fischer-Tropsch is given by M.E.
Dry in "Catalysis Science and Technology" (J.R. Anderson
and M. Boudart (eds.)) Vol. 1, Springer Verlag 1981.

In essence the Fischer-Tropsch synthesis takes
5 place over the metals iron, cobalt, nickel or ruthenium,
supported or unsupported, containing promoters or
additives which enhance activity or suppress unwanted
byproduct formation.

In the particular instance of the invention, a
10 component of the Fischer-Tropsch catalyst is a zeolite.
Zeolites are crystalline alumino-silicates which are
described in "Zeolite Molecular Sieves" by D.W. Breck,
John Wiley & Sons 1974.

The liquid products of the FT process may
15 conveniently be described as a four component mixture
comprising naphtha (b.p. C_5 to 195°C), kerosine (b.p. 195
to 235°C) and distillate (b.p. 235 to 315°C), and fuel
oil (b.p. > 315°C).

The presence of a high proportion of linear
20 hydrocarbons is desirable in the kerosine and distillate
fractions, which confer on the product a high cetane
number and a low octane number. On the other hand the
quality of the naphtha fraction is enhanced by the
presence of branched and unsaturated hydrocarbons and
25 aromatics which result in a higher octane number.

The major product of the classical FT process
is linear paraffins, and consequently the quality of the
naphtha fraction is unsatisfactory. Previous attempts to
enhance the quality of the naphtha fraction by
30 restructuring have resulted in concomitant undesirable
restructuring of the kerosine and distillate fractions.

Process of the Invention

It is an object of the present invention to provide a modified FT process which results in a preferential restructuring of the naphtha fraction,
5 compared with a minor restructuring of the kerosine and distillate fractions.

Consequently there is an improvement in quality of the naphtha without substantial deterioration in the quality of the kerosine and distillate fractions.
10 In one aspect the invention provides a process for conversion of synthesis-gas into a product which comprises three components, naphtha (b.p. C_5 to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C) in which the naphtha fraction is modified to
15 contain branched alkanes and alkenes. More particularly, the modified naphtha fraction contains not more than 60% linear paraffins, while the kerosine and distillate fractions contain more linear paraffins and olefins than are present in the naphtha fraction.
20 Synthesis-gas is a general term used for a gas comprising substantial portions of carbon monoxide and hydrogen. The gas may also contain carbon dioxide and water. Synthesis-gas can be made from any carbonaceous source, by the known processes of partial oxidation,
25 gasification or steam reforming. The relative concentrations of the gaseous components depends upon the source of the synthesis-gas and the process chosen. Sources for synthesis-gas include coal, oil shale, petroleum hydrocarbons and natural-gas.
30 In the process of the invention, no limits are placed on the composition of the synthesis gas however the composition will to some extent reflect the choice of source. For example, coal derived synthesis-gas is characterized by a relatively high carbon monoxide
35 content (ratio of hydrogen to carbon monoxide being typically ca 0.5 mole/mole), whereas for natural gas

derived synthesis-gas the hydrogen content is somewhat
higher (ratio of hydrogen to carbon monoxide being
typically ca. 2 or more).

The ratio of hydrogen to carbon monoxide is
5 also influenced by the technology chosen to produce the
synthesis-gas. For instance steam reforming of
natural-gas gives a hydrogen to carbon monoxide ratio of
3 or more whereas partial oxidation of the natural-gas
gives a ratio of 1.5 or less. Once produced the ratio of
10 hydrogen to carbon monoxide can be adjusted to any value
by separation or the use of the water-gas shift reaction.

We have been particularly interested in
natural-gas derived synthesis-gas as a means of utilizing
Australia's abundant natural-gas reserves, however the
15 process of the invention is not limited to the high
hydrogen content synthesis-gas usually derived from
natural-gas by steam reforming.

The Fischer-Tropsch synthesis converts
synthesis-gas into hydrocarbons ranging in weight from
20 methane to heavy waxes. The distribution of the
hydrocarbons produced is in accordance with the
Schulz-Flory distribution whereby the ratio (in mole
terms) of material of any given carbon number bears a
simple relationship to the material at the next highest
25 carbon number, this ratio being the Schulz-Flory Alpha
value (α).

$$\frac{\phi_{(n+1)}}{\phi_n} = \alpha$$

30 wherein ϕ_n and $\phi_{(n+1)}$ are respectively the number of
moles in carbon numbers n and n + 1, and is a constant
less than unity. The Schulz-Flory Alpha Value is a known

method of describing the product distribution in
Fischer-Tropsch synthesis, see for example U.S. Patent
4,595,703.

Now if alpha is ca. 0.6, substantially all the
5 hydrocarbon product produced (90%) will boil at less than
195°C i.e. be naphtha or light gases. If alpha is
greater than ca. 0.95 most of the product will be heavy
wax b.p. higher than 315°C. The process of the invention
relates to Fischer-Tropsch processes giving substantial
10 amounts of hydrocarbon boiling in the naphtha (C_5-195°C),
kerosine (195 to 235°C) and distillate (235 to 315°C)
ranges, and will thus apply to Fischer-Tropsch synthesis
with alpha values in the range 0.6 to 0.95 and more
preferably to 0.65 to 0.85, when the product contains
15 significant quantities of kerosine and distillate and is
not heavily laden with heavy-wax.

Classical Fischer-Tropsch catalysts comprise an
active metal (iron, cobalt, nickel or ruthenium) which
may be supported (for example on alumina or silica) and
20 promoted with small amounts of other materials; for
example iron catalysts are usually promoted with small
quantities of potassium, and cobalt catalysts can be
promoted with thoria. Many compositions of
Fischer-Tropsch catalysts are described in the
25 literature. The principal products of Fischer-Tropsch
synthesis are normal paraffins and olefins.

Zeolites constitute one component of the
Fischer-Tropsch catalyst pertinent to this invention.
Zeolite catalysts are well known in performing
30 shape-selective hydrocarbon transformations. Zeolites
have been described as components of Fischer-Tropsch
catalysts where they are said to bring about
shape-selectivity to the synthesis. In the prior art,
the use of zeolites to influence the product distribution
35 has been directed towards maximising the naphtha fraction
at the expense of the kerosine and higher fractions.

For example, Dwyer and Garwood in U.S. Patent
4,463,101 describe the use of an iron Fischer-Tropsch
catalyst in association with a high silica zeolite for
the conversion of synthesis-gas into olefinic naphtha.
5 This patent, like many others, utilises zeolites of the
ZSM-5 family. The ZSM-5 zeolite, with a ten-ring port,
has been found particularly useful in limiting the
synthesis product to the naphtha fraction and there are
many examples of its use for this purpose.
10   Other zeolites can also be used, for example
smaller port zeolites such as erionite or larger port
zeolites such as faujasites.

      Zeolites are more fully described by D.W. Breck
in "Zeolite Molecular Sieves" (Wiley 1974). Zeolites are
15 crystalline open pored structures with openings in the
range of molecular dimensions, which can allow the entry
and egress of simple molecules such as those found in
transport fuels to the interior of the crystal. Zeolites
are principally alumino-silicates but other elements can
20 substitute for the aluminium or silicon. Such elements
include gallium, germanium and phosphorus. Some of these
substituted materials are known by names other than
zeolites e.g. SALPOS which comprise open pored structures
of alumina, silica and phosphate. The term zeolite is
25 used here to include all such open structures which can
permit the entry and egress of molecules of the size
found in transport fuels.

      The Fischer-Tropsch synthesis can be performed
over a range of pressures, a wide range of space
30 velocities and over a wide temperature range. By
comparison to the influence of temperature, space
velocity and pressure only slightly influence the product
distribution. At low temperatures heavier materials are
favoured and as temperature is raised lighter material is
35 formed. In other words increasing temperature lowers the
alpha value. When combined with zeolites,

Fischer-Tropsch catalysts tend to be operated at
relatively high temperatures ($>250^{O}$C), typically 280°C
or 300°C. Under these conditions, the alpha value is
naturally low, independent of any shape selective action
5 of the zeolite.

The process of this invention requires that the
alpha value be preferably not less than ca. 0.65. This
places an upper limit on the temperature of operation at
about 270°C.

10   In order for the zeolite to be effective, the
temperature of the system will be required to be above
some limit typically ca. 220°C. Operation below this
limit, depending upon and probably peculiar to the
particular catalyst, may produce essentially
15 Fischer-Tropsch products as if the zeolite component were
absent; that is, not show branching selectivity as the
carbon number changes.

The process of the invention, in temperature
terms, is preferably carried out in the range 220 to
20 270°C, at GHSV and pressures optimum for the particular
catalysts, for example under the following conditions:

Temperatures:	220 to 270°C
Pressure:	0.1 MPa to 5 MPa, preferably 1 to 4 MPa
25 GHSV:	50 to 10,000, preferably 100 to 5000
Alpha:	0.60 to 0.95, preferably 0.65 to 0.85

Of these parameters, the value of alpha is more
important than the temperature.

The zeolite component of the Fischer-Tropsch
30 catalyst brings to the catalyst an acidic function, which
is placed in a restricted environment. Without being
bound by any theory, in order to be restructured, the
normal paraffins and olefins produced by the
Fischer-Tropsch component of the catalyst will need to

diffuse through the zeolite to the active centres within the zeolite crystals. This means there will be a diffusion limitation to the conversion of the unbranched hydrocarbons.

5   Restructing for the linear paraffins and olefins proceeds to produce an increase in the amount of branching in the chain. AT higher severities, further restructuring to aromatics and other cyclic species may occur. The requirement is that the amount of linear
10 product is significantly reduced in the naphtha fraction but restructuring will be less for the higher boiling fractions.

The choice of zeolite is an important aspect of the invention. Without wishing to be limited by any
15 theoretical considerations, we believe that the required action is one of chain length selectivity whereby lighter (b.p. to 195°C) paraffinic and olefinic hydrocarbons are able to diffuse to the active centres within the zeolite crystal more rapidly than are heavier (b.p. over 195°C)
20 paraffins and olefins. Such selectivity we intuitively expect not to be abrupt (although abrupt chain length selectivity has been observed in the cracking of normal paraffins over erionite), but a gradual change over the boiling range of the Fischer-Tropsch product.
25 Nevertheless, the point to be realised is that the lighter products (naphtha) diffuse more rapidly and are hence more reactive than the heavier products (kerosine and higher fractions).

Thus, the first principle in the selection of
30 the zeolite component is that normal paraffins and olefins can readily diffuse into the crystal. Upon reaching the active centre, the paraffins and olefins will be skeletally isomerized or further processed to branched aliphatics. These molecules must be able to get
35 out of the zeolite which defines the lower limit of pore size to be those corresponding to 10-ring windows.

The zeolite must also be capable of carrying an acid function and be stable under the condition of the FT synthesis.

Examples of zeolites fulfilling these
5 requirements are ZSM-5, and ZSM-11, Zeolite Y and dealuminised Zeolite Y. It would be expected that many other zeolite structures such as ZSM-12, mordenite, dealuminised mordenite and Zeolites X and L would be effective. This list is not meant to be limiting in any
10 way.

The optimisation of the relative quantities of the various components of the catalyst of the invention, Fischer-Tropsch metal (or metals), promoters, supports, zeolite, and binder and the optimisation of the
15 performance of the catalyst is easily performed by one skilled in the art.

The preferred Fischer-Tropsch metal is cobalt. One example of a catalyst employed according to the invention will contain 5 to 50% cobalt and 10 to 90%
20 zeolite, any balance being made up by promoters, inert supports and/or catalyst binders.

An important aspect of this invention is the consideration of the value of the Fischer-Tropsch products as hydrocarbon fuels or blends.
25 In classical Fischer-Tropsch, molecules with straight carbon-chains are the principal components, monomethyl isomers being present in small amounts. Such a product leads to good quality distillate and kerosine fractions which in consequence are of high value.
30 Unfortunately, this is not the case with the naphtha fraction where straight molecules lead to product of low octane number (typically ca. 40). Using zeolites in the catalyst, at high temperatures (ca. 280°C) gives a naphtha of improved octane value (e.g. 80 or more), but
35 little or no kerosine or distillate fraction is formed.

Fischer-Tropsch product is a broad boiling
range material and thus can be said to resemble crude
oil. Crude oils are subject to variation in quality, for
instance due to sulphur content. In the case of
5 Fischer-Tropsch product there is no sulphur present which
leads them to be ranked with the better crude oils.

Another important quality differential is based
on the reduction in the relative amount of straight chain
material in the naphtha cut, which increases the octane
10 number and so enhances the quality of the gasoline
product. The products of the invention have branched
paraffins and olefins present in the naphtha fraction.
The result is that a high quality naphtha is formed.

However, in the kerosine and distillate
15 fractions, the absence or low amounts of branched chain
material is considered important because if present in
these fractions they lead to a lower cetane number. The
products of the invention have comparatively low amounts
of branched chain material in the kerosine and distillate
20 fractions. Thus the high quality of Fischer-Tropsch
kerosine and distillate is maintained.

Fuel-oil (b.p. over 315°) is one of the least
useful fractions of crude oil and substantial quantities
have to be cracked into gasoline, especially in countries
25 like Australia with a high gasoline and low fuel-oil
demand. The products of the invention are low in
fuel-oil fraction, leading to the whole product being
easily processed by conventional oil refineries.

The product of the invention is thus a premium
30 quality synthetic crude oil.

The following examples illustrate the process
of the invention. In all of the examples, the feed is
synthesis gas with a v/v ratio of $CO:H_2$ of 1:2.

Example 1

This illustrates the synthesis of a simple Fischer-Tropsch catalyst (code FT18).

The zeolite, H-ZSM-5 (4.43g, $SiO_2/Al_2O_3 = 40$)
5 was impregnated with cobalt nitrate solution (2.44 g in 2.5 ml water). The catalyst was dried overnight at $90^{\circ}C$. The catalyst was formed into extrusions with the aid of acid washed bentonite (2/1, w/w, catalyst/bentonite), then fired at $500^{\circ}C$.

10 By mercury intrusion porosimetry the surface area was measured to be 16.2 m^2/g with a pore volume of 0.47 cc/g.

Analysis showed the catalyst contained Co_3O_4, 9.6%; Al_2O_3, 9.8%; Fe_2O_3, 1.3%; SiO_2, 72%; H_2O, 6.0%.
15 Before use, the catalyst was broken and sieved to size fraction 1-2mm.

Example 2

The catalyst (1.2 ml) of Example 1 was charged into a microreactor. The catalyst was pretreated at
20 $350^{\circ}C$ in hydrogen (100ml. min.$^{-1}$ at 0.1 MPa) for 16hr. The catalyst was cooled to a reaction temperature ($280^{\circ}C$). After synthesis the catalyst was reactivated in hydrogen at 350° before synthesis at $220^{\circ}C$ and then again before synthesis at $250^{\circ}C$. All syntheses were performed
25 at GHSV = 1000 hr^{-1} at 2MPa with a synthesis-gas ratio of 1.88/1, v/v, H_2/CO.

The results of the synthesis are given in Table 1.

TABLE 1

Run	FO22/3	FO23/3	FO21/3
Temperature (deg. C)	220	250	280
Time on Line (hr)	195	96	93
CO Conversion % (Average)	8	36	71
Alpha Value	0.82	0.74	0.58
n-paraffin Other products at:-			
C10	2.21	1.73	0.95
C13	1.82	1.97	0.92
C17	2.12	2.13	1.58

The run at 220°C shows little selectivity in the product as witnessed by the ratio of n-paraffins to other products at carbon numbers 10, 13 and 17. The conversion in this instance is also very low at 8%.

The run at 280°C produces a product very rich in naphtha (alpha value less than 0.6) and little selectivity is observed in the product.

At 250°C, the process of the invention is illustrated. The alpha value at 0.74 shows the product will contain reasonable quantities of kerosine and

distillate, obtained at reasonable conversion (36%).
Further as the weight of product increases so does the
amount of n-paraffin in the product.

Examples 3 to 6

5   These examples illustrate the invention, and
were carried out under the following conditions:
temperature 240°C; pressure 2MPa; GHSV 1000

Catalyst	CO Conversion (%)	α	n-Alkane proportions		
			C_9-C_{11}	$C_{11}-C_{13}$	$C_{13}-C_{18}$
3. 100 Co:500 ZSM-5(95)	88	0.84	0.36	0.42	0.49
4. 100 Co:1000 ZSM-5(95)	65	0.81	0.27	0.32	0.46
5. 100 Co:500 ZSM-5(95):500 SiO$_2$	67	0.85	0.51	0.57	0.67
6. 100 Co:18 ThO$_2$:1000 ZSM-5(95)	66	0.79	0.27	0.33	0.55

Example 7

20   This example shows that a critical temperature
is required to effect selectivity. Conditions are the
same as examples 3 to 6 with the exception that the
temperature is 230°C instead of 240°C.

Catalyst	CO Conversion (%)	α	n-Alkane proportions		
			C_9-C_{11}	$C_{11}-C_{13}$	$C_{13}-C_{18}$
as Example 3	70	0.79	0.52	0.51	0.60

Examples 8 to 12

These examples show the benefits of zeolites (8, 9 and 10) compared with other supports (11 and 12) in the process of the invention.

These examples were carried out under the following conditions:

temperature $250^{\circ}C$; pressure 2MPa; GHSV 1000

Catalyst	CO Conversion (%)	α	n-Alkane proportions		
			C_9-C_{11}	$C_{11}-C_{13}$	$C_{13}-C_{18}$
8. 100 Co:1000 ZSM-5(95)	69	0.68	0.24	0.26	0.29
9. 100 Co:1000 LZ-Y82[a]	47	0.78	0.52	0.56	0.64
10. 100 Co:1000 KWO42[b]	80	0.68	0.13	0.18	0.41
11. 100 Co:1000 Bentonite	83	0.72	0.72	0.66	0.60
12. 100 Co:1000 Al_2O_3	66	0.80	0.82	0.80	0.76

(a) commercial faujasite cracking catalyst

(b) highly dispersed ZSM-5

Example 13

This illustrates the use of dealuminised zeolite Y as a component of the catalyst of the invention. The zeolite Y had a silica/alumina ratio of 8. Conversion was carried out under the following conditions:

Temperature $250^{\circ}C$; pressure 2MPa; GHSV 1000

Catalyst	CO Conversion (%)	α	n-Alkane proportions		
			C_9-C_{11}	$C_{11}-C_{13}$	$C_{13}-C_{19}$
13. 100 Co:500HY(8):500 SiO_2	57	0.79	0.60	0.62	0.66

It will be clearly understood that the
invention in its general aspects is not limited to the
specific details referred to hereinabove.

CLAIMS:

1. Process for the catalytic conversion of synthesis-gas into a product which comprises naphtha (b.p. C_5 to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C) characterized in that the catalyst is a Fischer-Tropsch catalyst also containing a zeolite and the naphtha fraction contains 60% or less linear paraffins but the kerosine and distillate fractions contain more linear paraffins and olefins than found in the naphtha fraction.

2. Process according to Claim 1 in which the zeolite has a pore size corresponding to at least 10-ring windows and carries an acidic function.

3. Process according to Claim 1 carried out at a temperature in the range from 220°C to 270°C.

4. Process according to Claim 1 in which the product has a Schulz-Flory alpha value in the range 0.6 to 0.95.

5. Process according to Claim 4 in which the alpha value is in the range 0.65 to 0.85.

6. Process according to claim 1 in which the zeolite is chosen from the group consisting of the ZSM-5 family, ZSM-11, Zeolite Y and dealuminised Zeolite Y.

7. Process according to Claim 1 in which the zeolite is of the ZSM-5 family and the process is carried out under the following conditions:

Temperature	220 to 270°C
Pressure	0.1 MPa to 5 MPa
GHSV	50 to 10,000
Alpha value	0.60 to 0.95

8. Process according to Claim 1 in which the zeolite is of the ZSM-5 family and the process is carried out under the following conditions:

Temperature	220 to 270°C
Pressure	0.1 MPa to 4.0 MPa
GHSV	100 to 5000
Alpha value	0.65 to 0.85

9.   Process according to Claim 1 in which the catalyst contains 5 to 50% cobalt and 10 to 90% zeolite, any balance being made up by promoters, inert supports and/or catalyst binders.

10.   Process for the catalytic conversion of synthesis gas into a product which comprises naphtha (b.p. C_5 to 195°C), kerosine (b.p. 195 to 235°C) and distillate (b.p. 235 to 315°C) characterised in that the catalyst contains 5 to 50% cobalt and 10 to 90% zeolite of the ZSM-5 family; the process is carried out at a temperature in the range 220 to 270°C, pressure in the range 0.1 MPa to 5 MPa, and GHSV in the range 50 to 10,000; the product has an alpha value of 0.60 to 0.95 and the naphtha fraction of the product contains 60% or less linear paraffins but the kerosine and distillate fractions contain more linear paraffins and olefins than found in the naphtha fraction.

11.   A modification of the process according to claim 10 in which the zeolite is chosen from the group consisting of ZSM-11, Zeolite Y and dealuminised Zeolite Y.